

Pipe-bottle tests were conducted to investigate the permeation of benzene, toluene, ethylbenzene, and xylene (BTEX) compounds through 1-in.-diameter high-density polyethylene (HDPE) pipe exposed to gasoline-contaminated water and gasoline-contaminated unsaturated soil. Using the time-lag method, the concentration-dependent diffusion coefficients of BTEX compounds were estimated to be on the order of ~ 2 to $\sim 9 \times 10^{-9}$ cm²/s. Smaller pipes were more vulnerable to permeation than larger pipes, and pipes subject to periodic stagnation were more likely to exceed the maximum contaminant level of benzene than were pipes with continuous water flow. Under otherwise identical conditions, HDPE pipes buried in a soil of high organic matter were permeated to a lesser extent than pipes buried in a soil of low organic matter for exposure times exceeding 30 days.

Permeation of BTEX compounds through HDPE pipes under simulated field conditions

Polyethylene (PE) pipes have excellent abrasive-, impact-, and corrosion-resistance properties and are widely used in water service line connections and, to a lesser extent, water mains (Chevron Phillips Chemical Co., 2003). However, strong evidence from the literature and field studies suggests that organic contaminants permeate PE pipes and adversely affect the quality of drinking water in distribution systems. According to a survey completed in the 1980s, PE pipes were involved in 39% of total incidents of drinking water contamination resulting from permeation by organic contaminants (Thompson & Jenkins, 1987). Contamination by aromatics and chlorinated solvents in drinking water as a result of permeation through PE pipes was more likely after a period of water stagnation in the pipe (Holsen et al, 1991a). In a recent survey, 3 of 44 permeations involving drinking water service connections were associated with PE pipes, whereas the bulk of the incidents were associated with polybutylene (PB) pipes (Ong et al, 2008).

The permeability of organic compounds through PE pipes is attributed to the structural characteristics of PE. PE is characterized as a semicrystalline polymer, having both crystalline and amorphous regions. The crystalline zones act as impermeable barriers for diffusion, whereas the noncrystalline matrix (amorphous regions) is readily permeable because the polymeric chains in the amorphous areas are relatively “mobile”

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(Naylor, 1989). Because of the nonpolar nature of PE, lipophilic organic compounds can rapidly permeate through PE pipes, whereas PE pipes demonstrate excellent resistance to permeation by strongly polar compounds (Vonk, 1985).

Although it is well known that organic compounds readily permeate PE pipes (Thompson & Jenkins, 1987; Vonk, 1985), significantly less effort has been devoted to simulation of field contamination conditions; as a result, few data are available that can be applied to predict permeation behavior in the field. Vonk (1985) reported diffusion coefficients for a wide range of organic compounds in PE pipes, but his study focused on the permeation of a single compound from aqueous solutions under well-mixed conditions. Because permeation can occur either in the vadose zone or the saturated zone (FWR, 1992), aqueous exposure experiments alone are insufficient to simulate a comprehensive permeation behavior of pipes in the subsurface environment. Moreover, most chemical spills and contamination episodes in the field involve organic mixtures. The permeation characteristics of mixtures may differ widely from those of single organic compounds because of synergistic effects. Park and co-workers (1991) reported that organic chemicals that do not readily permeate PB pipes when present alone can have their permeability enhanced considerably when they are mixed with highly permeable organic chemicals. In addition, soil type and characteristics may have a significant effect on the permeation of organic compounds through pipe materials by implicitly determining the effective availability for permeation (Holsen et al, 1991b).

Gasoline leaks and spills account for nearly 90% of reported incidents of permeation of water distribution systems in the United States (Ong et al, 2008; Thompson & Jenkins, 1987). The objectives of the current study were first, to simulate the permeation of benzene, toluene, ethylbenzene, and xylene (BTEX) compounds into potable water in high-density polyethylene (HDPE) pipes from gasoline-contaminated groundwater as well as gasoline-contaminated unsaturated soil, and second, to determine permeation rates and diffusion coefficients necessary for developing empirical equations to predict permeation behavior under conditions of contamination that are commonly encountered in the field. The effects of organic matter in soil were also examined. Benzene was emphasized for predictive purposes because it has the highest diffusion coefficients and aqueous solubility and by far the lowest maximum contaminant level (MCL) established by the US Environmental Protection Agency for the BTEX compounds.

MATERIALS AND METHODS

Materials. Nominal 2.54-cm (1-in.) HDPE pipe, standard inside dimension ratio (SIDR) 9, was obtained from an HDPE pipe manufacturer.¹ Premium gasoline was purchased from a local gas station, and the concentra-

tions of benzene, toluene, ethylbenzene, *m*-xylene, and *o*+*p*-xylene in the gasoline were determined by gas chromatography to be 19.8, 75.9, 14.7, 33.7, and 32.5 g/L, respectively. Three types of soils—silica sand,² organic topsoil, and a mixture of sand and topsoil—were used in the experiments. The organic topsoil, which was purchased from a local store, was air-dried and then sieved to a fine-enough size to pass through a 2-mm sieve. Another soil was prepared by combining approximately equal parts of silica sand and dried, sieved, organic topsoil with a mixer.³ Triplicate samples were taken randomly from each prepared soil and analyzed for their important physical and chemical properties according to *Methods of Soil Analysis* (Klute, 1986; Page, 1986). The organic carbon content of the organic topsoil and the

The presence of reductive dehalogenation products (dibromoacetic acid, bromoacetic acid, and bromide) indicated that abiotic reduction at the pipe wall was the dominant tribromoacetic acid loss process.

sand-topsoil mixture was determined as 5.1 and 1.9%, respectively, and the organic carbon content of the silica sand was below the detection limit. The analysis for soil particle size distribution also indicated that all three soils were sand-dominated (93% or higher).

Apparatus. Experiments were conducted using a pipe-bottle apparatus (Figure 1), consisting of a 1-L glass bottle with HDPE pipe mounted horizontally through holes drilled in the glass. The connections between pipe and bottle were sealed with plastic epoxy⁴ and further covered by epoxy putty.⁴ The ends of the pipes were sealed with PTFE plugs. One of the PTFE plugs had a small hole that was plugged with a threaded brass plug to allow filling and draining of the water inside the pipe with a glass syringe. The bottle was capped with a PTFE-lined cap. The total surface area of PE pipe exposed to the bulk solution was approximately 81.9 cm². To simplify the experimental system and facilitate ease in handling the pipe-bottle apparatus, all experiments were conducted at room temperature (23 ± 1.5°C).

Exposure of HDPE pipes to gasoline-contaminated water. Gasoline-saturated water was prepared by mixing 350 mL of premium gasoline and 3.5 L of deionized water in a 4-L glass bottle for 48 h using a magnetic stirrer. (Several preliminary experiments indicated that a mixing time of 48 h was sufficient to produce a saturated solution.) Fresh gasoline-saturated water was prepared weekly throughout the study. The concentration of dissolved BTEX was ~150 mg/L, which was slightly higher

than the average value of 135 mg/L reported by other researchers for water saturated with gasoline of different grades (Cline et al, 1991). Benzene and toluene accounted for nearly 90% of total dissolved BTEX. Concentrations of 50, 10, and 1% of saturation were prepared by diluting the gasoline-saturated solution with deionized water. The BTEX concentrations in the four aqueous solutions typically reflected the concentration range of BTEX found in groundwater associated with gasoline spills and leaks.

For each experiment, the mini pipe-bottle apparatuses were filled with silica sand until the bottle was nearly full. Sodium azide (1.5 g) was added to inhibit potential biodegradation of BTEX and was thoroughly mixed with the sand by rotating the bottle. The bottle was loosely capped with a PTFE-lined cap in which a small hole was drilled to accommodate a PTFE tube that reached to the bottom of the bottle. Using a pump,⁵ aqueous gasoline solution was then introduced into the sand through the PTFE tubing from bottom to top until the bottle was full. The PTFE tube was removed along with the cap, and the bottle was then tightly capped with a PTFE-lined cap with no hole. The final water level was approximately 2 cm above the surface of the soil, with minimum headspace. The apparatuses were wrapped with aluminum foil to minimize photodegradation.

The silica sand and the aqueous solution were replaced each week with new sand and fresh aqueous gasoline solution to maintain relatively constant aqueous concentrations of BTEX in the bottle. BTEX concentrations in the soil-pore water were measured periodically. For sample collection, the pipe bottles were gently rotated several times and then allowed to sit undisturbed for 10 min. Liquids above the soils were collected in vials using a glass syringe and then centrifuged at 5,000 rpm for 10 min. These supernatant liquids were analyzed in the same manner as the pipe water samples and were considered to simulate contaminated groundwater in the field.

Exposure of HDPE pipes to unsaturated gasoline-contaminated soil. Four levels of gasoline-contaminated soil were prepared by spiking 1 kg of the sand-topsoil mixture with known amounts of premium gasoline and mixing the soil by rotating the soil container for one week. The volumetric moisture content of the soil was adjusted to approximately 10%, which was above the water content of soils equilibrated at a relative humidity > 98% (Holsen et al, 1991b). The amounts of BTEX sorbed onto the four soils were determined using methanol extraction and analyzed by gas chromatography. The total BTEX amounts in the four soils were found to be 32, 89, 388, and 1,216 mg/kg dry soil. Toluene and xylene were the major aromatic compounds in the soil, accounting for approximately 90% of the total BTEX.

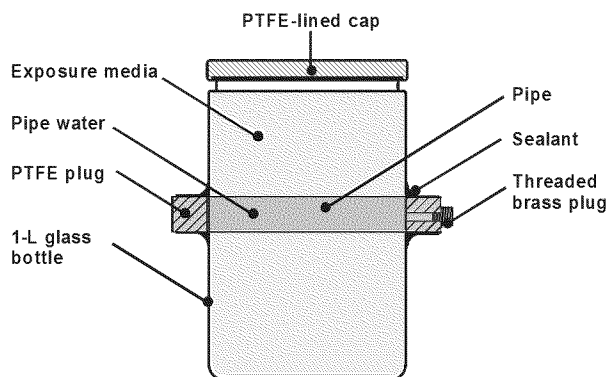
In these experiments, gasoline-contaminated soils were packed into the pipe-bottle apparatus. Under those conditions, mass transfer limitations in the soil might have

occurred when organic compounds were absorbed rapidly by the pipe wall, decreasing the concentration of organic compounds in the soil immediately adjacent to the pipe wall. Because of volatilization and diffusion, the concentration of BTEX in the soil and surrounding the pipes may not have remained constant over the experimental period. Throughout the experiments, water inside the pipes was drained for BTEX analysis and replenished with fresh deionized water. At the end of the experiments, soil samples were collected from the top layer (~4 cm above the pipe), middle layer (surrounding the pipe), and bottom layer (~4 cm below the pipe), and the residual BTEX in the soil was extracted by methanol and analyzed by gas chromatography.

Effect of soil organic matter on permeation. Pipe-bottle apparatuses were prepared using the three types of soil: silica sand, organic topsoil, and a sand-topsoil mixture. The soils were initially soaked with aqueous gasoline-saturated solutions. The experimental procedures were the same as described in simulated groundwater experiments except that the soils and aqueous solutions were not replenished. Soil-pore water and pipe water were collected periodically, and the BTEX concentrations were measured. To compensate for the liquid loss (~4 mL) from sampling and to maintain zero headspace, additional fresh gasoline-saturated water was added to each bottle immediately following sampling. The additions did not affect the concentration of BTEX in soil-pore water because the total capacity of soil-pore water (~400 mL) was much greater than the volume of fresh gasoline-saturated water added.

Gas chromatographic determination of BTEX. BTEX was determined using a gas chromatograph⁶ equipped with a packed column (1.8 m × 2 mm, 1% SP-1000 on 60/80 mesh⁷), a photoionization detector, and an automated purge-and-trap concentrator.⁸ The method detection limits for benzene, toluene, ethylbenzene, *m*-xylene, and *o*+*p*-xylene were 0.24, 0.24, 0.26, 0.29, and 0.53 µg/L, respectively.

FIGURE 1 Pipe-bottle apparatus



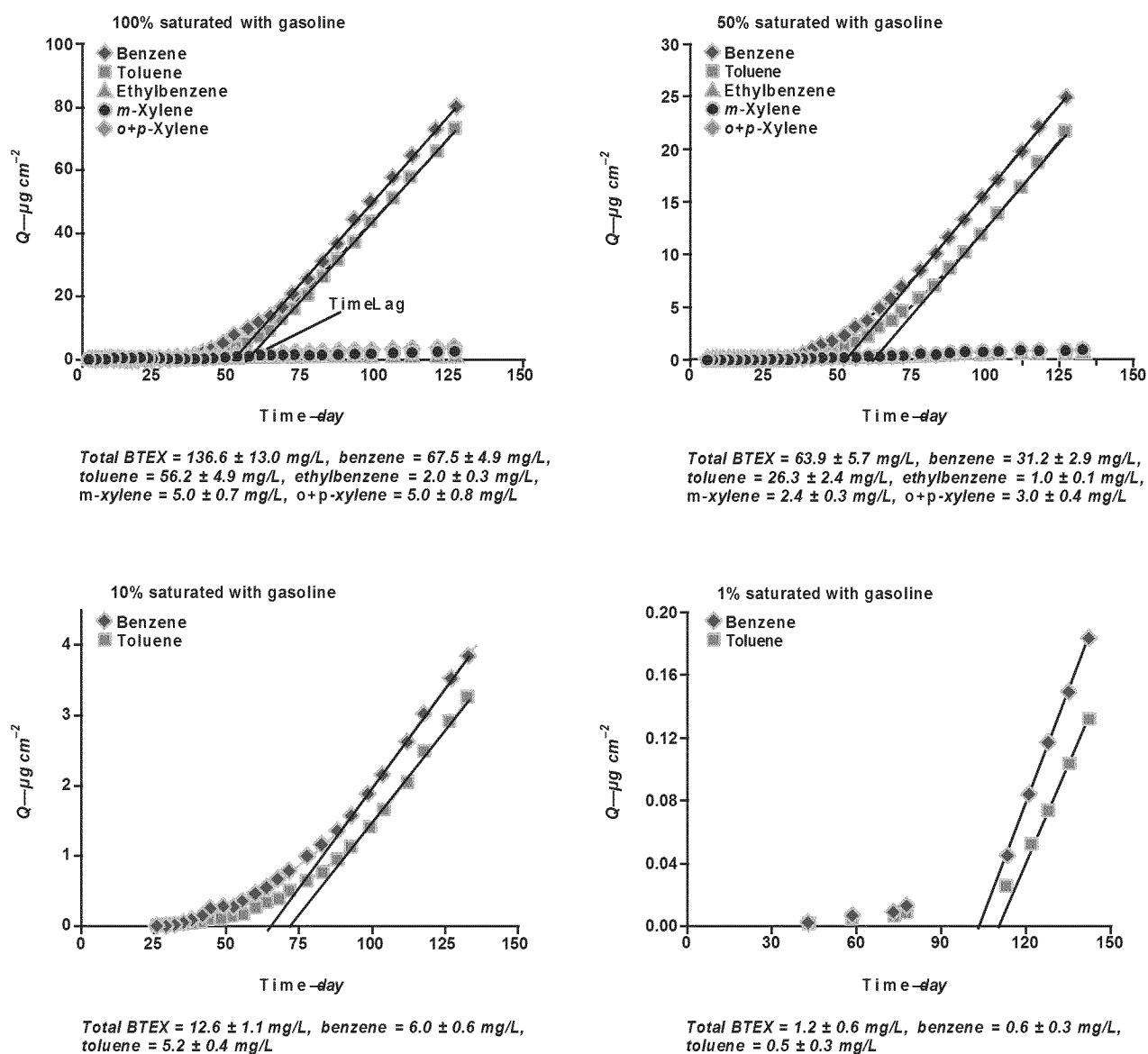
Determination of diffusion coefficients. The time lag, T_L , was determined using a plot of cumulative mass permeated per unit surface area, Q , versus time. T_L is the intersection with the time axis of the asymptote of Q versus t at steady-state conditions. If diffusion takes place in a hollow cylinder with inner and outer radii of a and b , respectively, the diffusion coefficients, D , can be estimated by Eq 1 (Crank, 1975):

$$D = \frac{b^2 - a^2 + (a^2 + b^2) \ln(\frac{a}{b})}{4 T_L \ln(\frac{a}{b})} \quad (1)$$

RESULTS AND DISCUSSION

Results for exposure of HDPE pipes to gasoline-contaminated water. Figure 2 plots the cumulative mass permeated per unit area for BTEX compounds at four levels of contamination. Permeation parameters are detailed in Table 1. Among BTEX compounds, benzene was the first to be detected in the pipe water, primarily because of the high concentration of benzene in the simulated groundwater and its relatively smaller molecular diameter. Once breakthrough occurred, the level of benzene in the pipe water quickly exceeded the MCL (5

FIGURE 2 Cumulative mass permeated per unit surface area Q for BTEX compounds in 1-in. SDR 9 HDPE pipes exposed to four concentrations of gasoline-contaminated water



BTEX—benzene, toluene, ethylbenzene, and xylene, HDPE—high-density polyethylene, SDR—standard inside dimension ratio

µg/L). The breakthrough of toluene was slightly behind that of benzene, whereas ethylbenzene and xylene were detected later and at much lower concentrations. Given the relatively high MCLs for toluene (1,000 µg/L) and ethylbenzene (700 µg/L), it took significant exposure times for the pipe water concentrations of these compounds to exceed the MCLs after breakthrough. Because

Three-dimensional laser-induced fluorescence techniques were applied for the first time to visualize and quantitatively investigate mixing in an ozone contactor used for water disinfection.

of the extremely high MCL for xylene (10,000 µg/L), its MCL was not exceeded within an experimental period of 140 days. Figure 2 also shows that breakthrough time increased with lower BTEX groundwater contamination, suggesting that higher bulk groundwater hydrocarbon concentrations lead to earlier breakthrough times.

Diffusion coefficients, D , of benzene and toluene at four levels of contamination were estimated using the time-lag method shown in Eq 1. Diffusion coefficients for benzene and toluene ranged from 1.8×10^{-9} to 3.6×10^{-9}

and 1.8×10^{-9} to 3.3×10^{-9} cm²/s, respectively, and are summarized in Table 2 for the different bulk exposure concentrations. For purposes of comparison, Table 2 includes diffusion coefficients from other studies.

As shown in Table 2, diffusion coefficients from the current study and other research were on the same order, approximately 10⁻⁹ cm²/s, despite differing polymer composition, crystallinity, concentration of contaminants, and experimental conditions. Diffusion coefficients for toluene obtained from this study using HDPE pipes were similar to those of Vonk's research (1985) using low-density polyethylene (LDPE) pipes. Table 2 also indicates that diffusion coefficients were concentration-dependent and increased with an increase in bulk exposure concentration. This concentration effect may be attributed to increased mobility of polymer segments resulting from increases in the average free volume in the polymer caused by the presence of the diffusing contaminant.

For each of four contamination levels, insignificant differences in the diffusion coefficients of benzene and toluene were found, which agreed with the results of Sangam and Rowe (2001) for HDPE geomembranes but conflicted with those of Joo and colleagues (2004) for HDPE geomembranes. In the latter study, the diffusion coefficient of benzene was found to be 1.5 times higher than that of toluene for a bulk concentration of 30 mg/L. One possible explanation for the nearly identical permeation of benzene and toluene detected in the current study might be the synergistic effect of organic

TABLE 1 Permeation parameters for benzene, toluene, ethylbenzene, and xylenes in 1-in. SDR 9 HDPE pipes exposed to gasoline-contaminated water

Exposure Conditions	Chemical	External Bulk Concentration mg/L	Breakthrough Time* day	Time That MCL Was Exceeded† day	Time Lag day	Steady-state Permeation Rate µg/cm ² /d
100% Saturated with gasoline	Benzene	67.5 ± 4.9	13	14	51	1.044
	Toluene	56.2 ± 4.9	20	39	55	1.011
	Ethylbenzene	2.0 ± 0.3	41	94	68	0.020
	<i>m</i> -Xylene	5.0 ± 0.7	41		68	0.047
	<i>o</i> + <i>p</i> -Xylene	5.0 ± 0.8	41		67	0.047
50% Saturated with gasoline	Benzene	31.2 ± 2.9	17	17	52	0.344
	Toluene	26.3 ± 2.4	23	44	61	0.325
	Ethylbenzene	1.0 ± 0.1	48	133	76	0.008
	<i>m</i> -Xylene	2.4 ± 0.3	48		76	0.017
	<i>o</i> + <i>p</i> -Xylene	3.0 ± 0.4	48		74	0.017
10% Saturated with gasoline	Benzene	6.0 ± 0.6	26	26	64	0.057
	Toluene	5.2 ± 0.4	29	79	72	0.052
1% Saturated with gasoline	Benzene	0.6 ± 0.3	43	46	104	0.0046
	Toluene	0.5 ± 0.3	43		110	0.0042

HDPE—high-density polyethylene, MCL—maximum contaminant level, SDR—standard inside dimension ratio

*Breakthrough time is defined as the time a chemical takes to permeate through the pipe material to be detected in pipe water.

†The mass permeated per unit area (Q_{MCL}) at which the concentration in the pipe-water would reach the MCL was calculated. The time that the MCL was exceeded for each testing condition was then estimated by interpolating the Q_{MCL} in the permeation curves as shown in Figure 2. Blanks indicate that MCL was not exceeded within the experimental period of approximately 140 days.

compounds on permeation. Most of the studies reported in Table 2 were based on the permeation of a single organic compound in aqueous solution through the polymeric material, whereas the current study used gasoline-contaminated water, which is a mixture of organic compounds. The presence of benzene with toluene may enhance the diffusion of toluene through HDPE pipes. Synergistic effects were also observed in the study by Park and co-workers (1991) in which toluene permeation through PB pipe was considerably enhanced by the presence of trichloroethylene.

The steady-state permeation rates, P_m ($\mu\text{g}/\text{cm}^2/\text{d}$), were strongly dependent on the bulk (external) concentration, C_{bulk} (mg/L), in the soil-pore water. On the basis of the measured data, two empirical correlation equations, Eqs 2 and 3, were obtained:

$$P_m = 0.0079C_{\text{bulk}}^{1.1323} \text{ for benzene} \quad (2)$$

$(R^2 = 0.998, n = 4, \text{SE} = 0.06)$

$$P_m = 0.0087C_{\text{bulk}}^{1.1444} \text{ for toluene} \quad (3)$$

$(R^2 = 0.997, n = 4, \text{SE} = 0.07)$

Eq 2 was used to estimate the concentrations of benzene in the pipe water for a given bulk contaminant concentration after a period of stagnation. Water stagnation, representing the worst-case scenario, typically occurs during the night in service lines of residences and office buildings. The concentration of contaminant in pipe water, C_{pw} , can be estimated by Eq 4:

$$C_{\text{pw}} = \frac{M}{V} \quad (4)$$

$$P_m \times \left[\frac{\pi \times \text{OD} \times L}{4 \times \pi \times \text{ID}^2 \times L_T} \right] \times C_{\text{bulk}} \times t = \frac{4 \times \pi \times f(C_{\text{bulk}}) \times \text{OD} \times L_C \times t}{\text{ID}^2 \times L_T}$$

in which M is the total mass of permeated contaminant (μg), V is the volume of water in the pipe (L), t is the period of stagnation (day), L_C is the length of contaminated pipe (cm), L_T is the total length of pipe (cm), and ID and OD are the inside and outside diameters, respectively, of the pipe (cm). As described previously, P_m is a function of the bulk concentration of con-

TABLE 2 Comparison of diffusion coefficients obtained from the current study with those from previous studies

Organic Chemical	Materials	Exposure Concentration mg/L	Diffusion Coefficient $\times 10^{-9} \text{ cm}^2/\text{s}$	Reference
Toluene	HDPE pipe Wall thickness: 3.1 mm	56.2 \pm 4.9	3.4	Current study
		26.3 \pm 2.4	3.0	
		5.2 \pm 0.4	2.6	
		0.5 \pm 0.3	1.8	
Toluene	LDPE pipe Wall thickness: 3.5 mm	91 \pm 16	4.7*	Vonk, 1985
		49 \pm 11	3.9*	
		31 \pm 5	3.9*	
		2.9 \pm 1.3	3.5*	
Toluene	HDPE geomembrane Thickness: 2.0 mm	30	3.3	Joo et al, 2004
Toluene	HDPE geomembrane Thickness: 0.76 mm	100	5.3	Park et al, 1996
		50	3.6	
		10	3.2	
Toluene	HDPE geomembrane Thickness: 2.0 mm	2	3.0	Sangam & Rowe, 2001
Benzene	HDPE pipe Wall thickness: 3.1 mm	67.5 \pm 4.9	3.6	Current study
		31.2 \pm 2.9	3.5	
		6.0 \pm 0.6	2.9	
		0.6 \pm 0.3	1.8	
Benzene	HDPE geomembrane Thickness: 2.0 mm	30	8.5	Joo et al, 2004
Benzene	HDPE geomembrane Thickness: 2.0 mm	2	3.5	Sangam & Rowe, 2001

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HDPE—high-density polyethylene, LDPE—low-density polyethylene

*Calculated on the basis of the permeation data in the reference

taminant in the soil-pore water, $f(C_{bulk})$, as indicated in Eq 2.

To simplify the calculation, the ratio of L_C to L_T (which would be the relative proportion of contaminated pipe) was arbitrarily set to four values (1:1, 1:5, 1:10, and 1:20), and the period of stagnation, t , was set to 8 h. With these simplifying conditions, the estimated bulk concentrations, C_{bulk} , (at steady-state permeation) that would result in exceeding the benzene MCL of 5 $\mu\text{g/L}$ in a 1-in. SDR 9 iron pipe size HDPE pipe for a stagnation period of 8 h were ~1, 4, 8, and 15 mg/L, corresponding to L_C -to- L_T ratios of 1:1, 1:5, 1:10, and 1:20, respectively. For practical purposes, there is no concentration of benzene at which HDPE pipe is immune from permeation. Therefore, in the event of a known gasoline or solvent spill in the vicinity of an HDPE service line, immediate corrective action should be taken because the MCL for benzene will likely be exceeded quickly. Replacement with copper is the most commonly used corrective action in such circumstances (Ong et al, 2008).

Under normal distribution conditions, the contaminant concentration will be affected by the water flow rate in the pipe. Assuming full pipe flow and complete mixing of the permeated contaminant in the pipe water, the concentration of benzene in pipe water, C_{pw} , can be estimated by Eq 5:

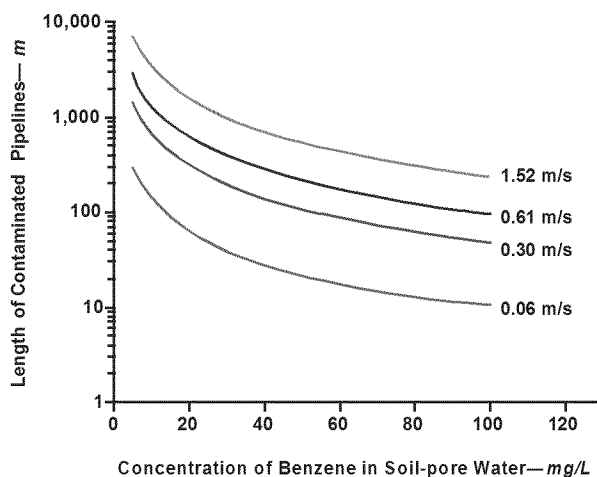
$$C_{pw} = \frac{M}{V} \quad (5)$$

$$P_m \times \frac{\pi \times OD \times L}{q \times t} \times C \times t = \frac{A \times f(C_{bulk}) \times OD \times L_C}{ID^2 \times v}$$

in which q is the water flow rate (cm^3/d) and v is the average water flow velocity (cm/d). Typically, the average water flow velocity recommended for plastic pipes, v , ranges from 0.06 to 3.7 m/s (Chevron Phillips Chemical Co., 2003). By setting the average water flow velocities at four values (0.06, 0.30, 0.61, and 1.52 m/s), the length of contaminated pipelines, L_C , required (at steady-state permeation) to exceed the MCL of benzene was estimated for a specific bulk concentration. Results are shown in Figure 3.

Figure 3 indicates that only very low water flow velocities (< 0.3 m/s) pose a risk of exceeding the MCL for benzene under the conditions of full pipe flow. To exceed the benzene MCL would require a contaminated pipeline more than 100 m in length and a bulk concentration of more than 40 mg/L if the water flow velocity is 0.3 m/s or greater. When the bulk concentration is below 10 mg/L and the length of contaminated pipe is < 150 m, it is expected that the concentration of benzene in pipe water would be below the MCL for any typical water flow velocity. Because of the effect of dilution, the hydrocarbon concentrations in HDPE pipes with water flow would be significantly less than those for conditions of stagnation.

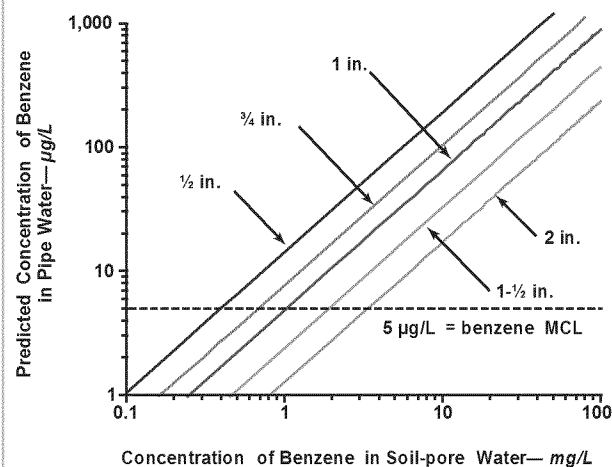
FIGURE 3 Length of contaminated pipe required to exceed the benzene MCL (5 $\mu\text{g/L}$) in pipe water for various bulk concentrations and water flow velocities for 1-in. SDR 9 HDPE pipe*



HDPE—high-density polyethylene, MCL—maximum contaminant level, SDR—standard inside dimension ratio

*Assumes the ratio of the length of contaminated pipe to total pipe length = 1

FIGURE 4 Predicted concentration of benzene in pipe water for various bulk concentrations after 8-h stagnation for SDR 9 series of HDPE pipe*



HDPE—high-density polyethylene, MCL—maximum contaminant level, SDR—standard inside dimension ratio

*Assumes the ratio of the length of contaminated pipe to total pipe length = 1

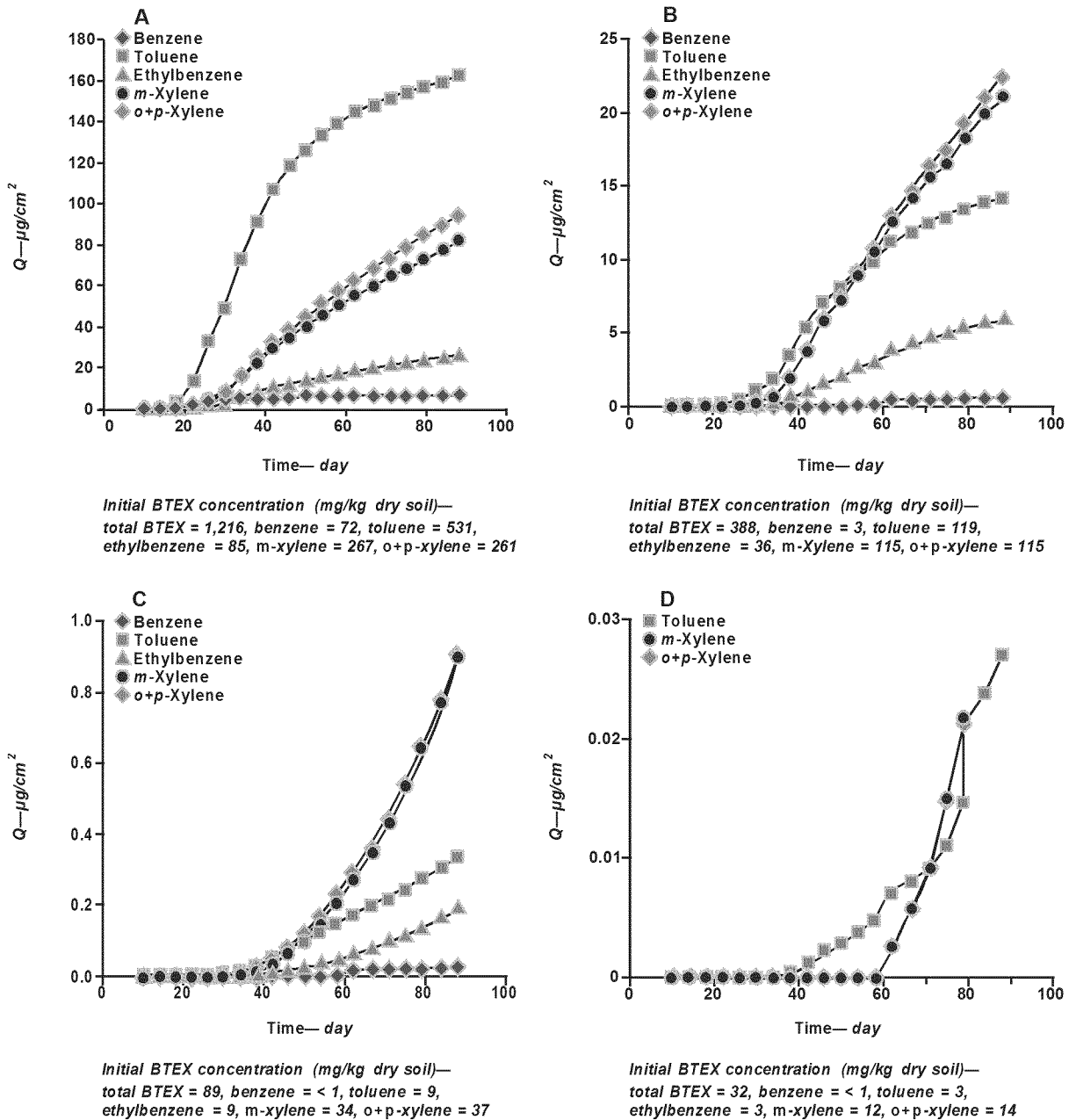
To predict the permeation behavior of contaminants for pipes with varied dimensions, the ID and OD in Eq 4 are known for a specific pipe size, but the steady-state permeation rate, P_m , must be corrected for the effects of dimension. On the basis of the physicochemical theory of permeation (Crank & Park, 1968), P_m can be expressed as in Eq 6:

$$P_m = C_{bulk} \frac{P_C}{l} = C_{bulk} \frac{DS}{l} \quad (6)$$

in which P_C is the permeation coefficient (cm^2/s), S is the solubility (dimensionless), and l is the pipe wall thickness (cm).

S describes the partition of contaminant between the bulk solution and the polymeric material and, in principle,

FIGURE 5 Cumulative mass permeated per unit surface area Q for BTEX compounds in 1-in. SIDR 9 HDPE pipes exposed to four concentrations of gasoline-contaminated soils



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BTEX—benzene, toluene, ethylbenzene, and xylene, HDPE—high-density polyethylene, SIDR—standard inside dimension ratio

is a constant for a given contaminant–polymer pair. There is disagreement with respect to whether D is dependent on the polymer thickness (Park et al, 1996). Generally, it is believed that D is independent of polymer thickness because D is determined only by the chemical characteristics of the polymer, the concentration (activity) of the contaminant compound, and the interactions between the contaminant and the polymer. However, other researchers investigated the effects of thickness on diffusion coefficients for HDPE geomembranes exposed to methylene chloride, toluene, trichloroethylene, and *m*-xylene and found that the diffusion coefficients decreased by 28 to 36% when the thickness increased from 0.76 to 2.54 mm at an initial concentration of 100 mg/L (Park et al, 1996). In the current research, D was assumed to be a constant for various pipe sizes because this assumption would be conservative (but safe) to predict the permeation risk for large pipe dimensions. For different pipe sizes, therefore, P_m is a function of only the wall thickness of pipe, l . The steady-state permeation rate for a specific pipe dimension can be deduced by Eq 7:

$$P_{mp} = P_{ms} \frac{l_s}{l_p} \quad (7)$$

in which P_{mp} is the predicted steady-state permeation rate for the wall thickness of l_p , and P_{ms} is the known steady-state permeation rate for the wall thickness of l_s . With known wall thickness, ID, and OD, the corresponding concentration of benzene in pipe water was estimated after 8-h stagnation for the SDR 9 series of HDPE pipes under various bulk concentrations (Figure 4).

Compared with large-size pipes, small-size pipes were more vulnerable to permeation (Figure 4). The higher susceptibility of small-size pipes to permeation is supported by the findings of a study of real permeation incidents that reported all permeation incidents for service lines were associated with pipe – 1 in. in diameter (Holsen et al, 1991a). For the same bulk concentration, the concentration of contaminant in pipe water decreases with increasing pipe size, mainly because of the increase of wall thickness and the resulting decrease in permeation rate.

Results for exposure of HDPE pipes to unsaturated gasoline-contaminated soil. Figure 5 plots the cumulative mass permeated per unit area, Q , for BTEX compounds at four levels of contamination. Toluene and xylenes were the major compounds detected in the pipe water, whereas the permeation of benzene through pipes was

TABLE 3 Permeation parameters for toluene, ethylbenzene, and xylenes in 1-in. SDR 9 HDPE pipes exposed to gasoline-contaminated soils

Chemical	External Bulk Concentration mg/kg dry soil	Breakthrough Time* day	Time That MCL Was Exceeded† day	Time Lag day	Steady-state Permeation Rate μg/cm ² /d	Diffusion Coefficient × 10 ⁻⁹ cm ² /s
Toluene	531	10	14	20	5.1	9.3
	119	14	28	30	0.43	6.1
	9	26		34	0.0061	5.4
	3	42		69	0.0014	2.7
Ethylbenzene	85	18	22	22	0.5	8.4
	36	22	41	32	0.12	5.8
	9	38		53	0.0054	3.5
	3					
<i>m</i> -Xylene	267	14	26‡	23	1.5	8.1
	115	18		33	0.43	5.7
	34	30		55	0.027	3.4
	12	62		65	0.0016	2.9
<i>o</i> + <i>p</i> -Xylene	261	14	26‡	23	1.7	8.1
	115	18		33	0.43	5.7
	37	30		55	0.027	3.4
	14	62		66	0.0016	2.8

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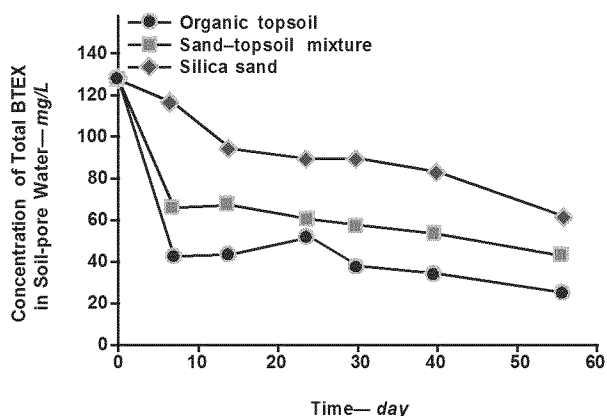
HDPE—high-density polyethylene, MCL—maximum contaminant level, SDR—standard inside dimension ratio

*Breakthrough time is defined as the time a chemical takes to permeate through the pipe material to be detected in pipe water.

†Mass permeated per unit area in corresponding to MCL was used to estimate the time when MCL was exceeded. Blanks indicate that MCL was not exceeded within the experimental period of approximately 90 days.

‡Determined according to the MCL for total xylene of 10 mg/L

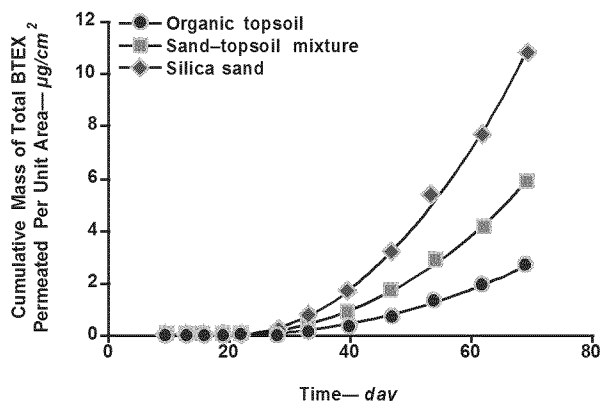
FIGURE 6 Concentration of total BTEX in soil-pore water versus exposure time



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BTEX—benzene, toluene, ethylbenzene, and xylene

FIGURE 7 Cumulative mass of total BTEX permeated per unit area versus exposure time



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BTEX—benzene, toluene, ethylbenzene, and xylene

insignificant. These observations were consistent with results reported from other permeation incidents (Holsen et al, 1991a). In three reported incidents involving gasoline, toluene permeated to the greatest degree, followed by xylenes, ethylbenzene, and benzene (in the same order as shown in Figure 5, part A), whereas in the other cases associated with gasoline, xylenes permeated more readily, followed by toluene and ethylbenzene (in the same order shown in Figure 5, parts B and C). Holsen and co-workers (1991a) attributed the low permeation of benzene to its relatively higher polarity. The properties

of polarity, however, cannot explain the higher and faster permeation of benzene (compared with the other BTEX compounds) when pipes were exposed to free gasoline or gasoline-contaminated water. As indicated in the current study, one possible reason is the relatively low benzene concentration remaining in the soils. This low concentration in the soils is attributable to benzene's high volatility, which gives it the lowest soil sorption affinity among the BTEX compounds (Zytner, 1994). In gasoline-contaminated groundwater, however, a relatively high concentration of benzene is generally detected because of its high solubility in water (Cline et al, 1991). From the perspective of permeation risk, therefore, plastic pipes buried in the water-saturated zone will be more easily permeated by benzene than those in the vadose zone. The case of benzene demonstrates that knowledge of environmental fate and transport is essential for evaluating the potential permeation risk of contaminants because the distribution of chemicals among environmental media determines the contaminant levels that plastic pipes might encounter in the field.

In the unsaturated soil, plastic pipe permeation was believed to occur from the vapor phase (Holsen et al, 1991b; Park et al, 1991). The current study did not collect vapor samples for BTEX analysis, and thus the exact concentration of BTEX in soil gas was unknown during the experimental period. At the end of the experiments, soil samples were taken from different positions (top, middle, and bottom) of the glass bottle, and the BTEX concentrations in the soils were found to be relatively uniform. For each of the four contamination levels, however, more than 90% of total BTEX in soils was lost over the entire experimental period of three months. The loss of toluene was relatively higher than that of xylene. The losses were mainly attributable to sorption/diffusion into the pipe and volatilization. Generally, the diffusion coefficients of organic compounds in the vapor phase through soil pores are several orders of magnitude larger than the diffusion coefficients through plastic pipes (Holsen et al, 1991b). Therefore, the mass transfer in soils may be rapid enough to hinder the development of a concentration gradient in the soils. The drop of BTEX concentration in soils indicated that the pipes were exposed to variable contaminant levels, which resulted in permeation curves that differed from those obtained with constant exposure concentrations. As shown in Figure 5, parts A and B (initial BTEX concentrations of 1,216 and 388 mg/kg, respectively), the permeation curves, especially for toluene, flattened out at later time periods. However, Figure 5, parts C and D, still showed a linear increase of cumulative mass permeated per unit area over time after steady-state permeation was reached—a typical curve predicted by permeation theory.

The time-lag approach cannot be used to estimate the diffusion coefficients of BTEX for this case because the experimental conditions did not meet the requirement

of “constant exposure concentration.” However, it may be reasonable to assume that the exposure concentrations did not significantly decrease at the early time period, and thus it is still possible to apply the time-lag method to calculate the diffusion coefficients based on the early breakthrough data. The first 50 days of data were used to estimate the diffusion coefficients for the individual BTEX compounds as shown in Figure 5, parts A and B. The permeation parameters for toluene, ethylbenzene, and xylene under the test conditions are summarized in Table 3.

Generally the diffusion coefficients, D , in Table 3 were of the same order of magnitude as those found in the

According to a survey completed in the 1980s, polyethylene pipes were involved in 39% of total incidents of drinking water contamination resulting from permeation by organic contaminants.

aqueous experiments (10^{-9} cm²/s), were concentration-dependent, and showed signs of synergistic effects. The synergistic effect was demonstrated by the diffusion coefficients of the three xylene isomers. In a previous study of HDPE geomembranes (Saleem et al, 1989), significant differences in the diffusion coefficients were detected for the three xylene isomers because of the effect of molecule structure (shape) on diffusion. In the current study, however, the three compounds had identical permeation characteristics when they coexisted in the soils. No previous study specifically investigated the permeation of organic contaminants through PE pipe buried in unsaturated soil. In addition, comparing the diffusion coefficients obtained from the three permeation tests (free product gasoline, gasoline-contaminated water, and gasoline-contaminated unsaturated soil) on the basis of the values of activity is a challenge because of the lack of consistent definitions of activity (Park et al, 1991).

Results for effect of soil organic matter on permeation. Sorption of BTEX into the soil organic matter was rapid, as shown in Figure 6. BTEX in the soil-pore water for the organic topsoil and sand-topsoil mixture dropped dramatically within the first week (mainly because of sorption to the soil) and then decreased slowly (mainly because of sorption/diffusion into the pipe and volatilization losses). Under otherwise identical initial conditions, the BTEX concentration in soil-pore water was lowest in the organic topsoil, which had the highest organic carbon content (5.1%), intermediate in the sand-topsoil mixture (1.9% organic carbon), and highest in silica sand, which had an insignificant organic carbon content. The different BTEX concentrations

were attributed to different BTEX sorption capacities for different types of soil. The higher organic matter in the organic topsoil resulted in greater soil uptake of BTEX and a significant decrease of BTEX concentrations in the soil-pore water (Chiou & Peters, 1981).

As demonstrated previously, the rate at which BTEX permeated HDPE pipes was strongly dependent on the external bulk concentration. The sorption of BTEX by soils decreased the BTEX concentration in the soil-pore water and thereby decreased the rate of permeation (Figure 7). The breakthrough times of benzene for silica sand, sand-topsoil mixture, and organic topsoil were 13, 16, and 19 days, respectively. After two months of exposure, the cumulative mass of BTEX permeated per unit area through the pipe buried in silica sand was nearly twice that of the sand-topsoil mixture and four times that of organic topsoil. However, high soil organic matter cannot be relied on to protect pipes from permeation because such soils eventually will reach their maximum adsorption capacities under field conditions. The effects of soil organic matter on permeation found in the current study were consistent with results of research on the permeation of organic contaminants through PB pipes (Holsen et al, 1991b).

CONCLUSIONS

On the basis of analysis of experimental results, several conclusions can be drawn.

HDPE pipe was rapidly permeated when exposed to gasoline-contaminated water or gasoline-contaminated unsaturated soils. Benzene and toluene accounted for nearly all the total BTEX that permeated into the pipe water when pipes were buried in the silica sand saturated with gasoline-contaminated water. Toluene and xylenes were the major compounds detected in the pipe water when pipes were buried in the gasoline-contaminated unsaturated soils.

With the use of the time-lag method, the diffusion coefficients of BTEX compounds were estimated to be on the order of ~ 2 to $\sim 9 \times 10^{-9}$ cm²/s. The diffusion coefficients were concentration-dependent and might be influenced by the synergistic effect of organic mixtures.

The steady-state permeation rates of benzene and toluene through HDPE pipe were logarithmically dependent on the external bulk concentration. Predictions using the empirical equations indicated that small-size pipes were more vulnerable to permeation than large-size pipes, and pipes with water stagnation periods posed a much greater risk of exceeding the benzene MCL relative to pipes with continuous water flow. Immediate corrective action should be taken in the event of a known spill of gasoline or organic solvents in the vicinity of an HDPE service line.

HDPE pipes buried in soils of high organic matter were permeated to a lesser extent than pipes buried in a soil of low organic matter. This is attributable to the

sorption of organic compounds by the organic matter, resulting in a lower soil-pore water concentration, compared with soils containing low amounts of organic matter. However, high organic matter in soil cannot be relied on to protect pipes from permeation because such soils eventually will reach their maximum adsorption capacities under field conditions.

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FOOTNOTES

- ¹SIDR 9 IPS NSF PW PE3408, ASTM-D2239-81, Endot Industries, Rockaway, N.J.
- ²Granusil 4030, UNIMIN Corp., Portage, Wis.
- ³Hobart Corp., Troy, Ohio
- ⁴Loctite®, Henkel Technologies, Rocky Hill, Conn.
- ⁵Masterflex, Cole-Parmer, Vernon Hills, Ill.
- ⁶Tracor 540, Tracor Instruments Austin, Inc., Austin, Texas
- ⁷Carbopack B, Sigma-Aldrich, St. Louis, Mo.
- ⁸Tekmar LSC2/ALS, Teledyne Tekmar, Mason, Ohio

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